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PROPAGATION OF SUPERSONIC WAVES IN LIQUID MIXTURES AND INTERMOLECULAR FORCES*

1. ALCOHOLS IN WATER

By RAM PARSHAD, M.Sc.

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ABSTRACT. In this paper is reported measurements on supersonic velocities, and compressibilities of mixtures of alcohols and water. Some quite new results are obtained. The velocity concentration curves show maxima and compressibility concentration curves show minima.

For the first time the theory of molecular force fields has been applied to sound problems and is first shown why the compressibilities are always lower than expected in ideal cases and later quantitative treatment is given whereby the percentage of the mixtures for minima of compressibilities is calculated.

In the case of methyl and ethyl alcohols in water the agreement between theory and experiment is good, whereas in propyl alcohol-water mixture there is a signifiaant divergence between the two values. This divergence has also been explained.

The basic idea employed in the above treatment is that though both alcohols and water are associated liquids, but when they are mixed, they destory each other's associations and a random motion and distribution of molecules prevail.

INTRODUCTION

The case of liquid mixtures is an important study in theory of liquids. Much work has been and is being done in various branches, *e.g.*, dielectric polarisation, heat of mixing, solubility, partial pressures, infra-red absorption spectra, but as yet we are far from any final solution of the problem. The determination of velocities and hence the compressibilities of the mixtures is expected to throw appreciable light on the state of cohesion as a function of molecular fields of liquids and also the structure of molecules as derived from the resulting intermolecular action.

Wilson and Richards [1] and Parthasarathy [2] have reported some observations on supersonic velocities and compressibilities of mixtures, without, however, any basic attempts at an explanation of their results.

We report, in this paper and in the following ones, investigations on various classes of mixtures. Some very new and interesting results have been found. In mixtures of alcohols and water there are maxima of velocity and minima of compressibility. In other mixtures have been found minima of velocity and points of inflection.

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In this paper and the succeeding, attempt is made to explain and discuss the results obtained by the author as well as those obtained by other workers.

EXPERIMENTAL

The well-known Debye-Sears method of diffraction of light by supersonics which has been set up in this laboratory by Dr. A. K. Dutta was employed to find the velocities. The green light of 5460 Å of mercury was used and the supersonic vibrations as obtained by means of a quartz crystal of frequency 3×10^6 cycles connected to the output of a suitable valve-transmitting circuit were used to produce the diffraction pattern. The quartz was always immersed in a constant liquid (xylol) and the vibrations to the liquid under investigation were transmitted through a mica window.

Great care was taken in temperature control. Round the vessel containing the liquid-mixtures and the oscillating quartz immersed in the xylol bath, was a water-bath, which was stirred continuously by a motor-driven stirrer and this bath contained a thermostat to keep the temperature at any constant value above the room temperature. The temperature was read by means of a mercury thermometer graduated to tenth of a degree. The maximum departure in rare cases from the constant value might be taken as .05°C, which however is far below the value which might in any way tend to vitiate the results. In general the maximum departure was .02°C. The spectra were photographed and measurements were made by means of Hilger comparator, reading accurately to 10^{-4} cms., of as many orders as possible and then the length of separation of the first order was deduced.

Two independent observations were taken for each mixture and in each observation three photographs were taken. The absolute velocities in the mixtures were found by comparing with the velocity in water. The velocity in water at the paticular temperature was taken from a graph plotted from the values of velocities at different temperatures for water taken from Handbuch des Experimental-physik, Vol XVII.

The velocity in any mixture was then found very simply by

$$\frac{V_m}{V_w} = \frac{d_w}{d_m}$$

where V_w is velocity in water,

V_m ,, any mixture,

d_w is length of separation of 1st order spectrum in water,

d_m is length of separation of 1st order spectrum in the mixture.

The adiabatic compressibilities of the mixtures were found from the relation,

$$V = \sqrt{\frac{1}{\beta\rho}}$$

where V is velocity in centimeteres per second,
ρ is density in gms. per c.cm..,
β is adiabatic compressibility in absolute units.

EXPERIMENTAL RESULTS

TABLE I

Liquid Ethyl Alcohol and Water

Temperature 32°.60C

No.	Volume % of alcohol in total of mixture	Density (gm./cc.)	Velocity (metre per sec.)	Adiabatic compressibility $\times 10^{-6}$
1	0	.995	1508	44.2
2	10	.987	1557	41.8
3	25	.968	1606	40.1
4	50	.9235	1508	47.6
5	75	.862	1334	65.2
6	90	.819	1225	81.4
7	100	.782	1138	98.8

TABLE II

Liquid Methyl Alcohol and Water

Temperature 26°.00C

No.	Volume % of alcohol in total of mixture	Density (gm./cc.)	Velocity (metre per sec.)	Adiabatic compressibility $\times 10^{-6}$
1	0	.9968	1500	44.59
2	18.6	.9700	1563	42.25
3	32.55	.9568	1573	42.47
4	46.5	.9263	1531	46.10
5	65.1	.8879	1423	55.58
6	80.55	.8496	1305	69.11
7	93	.8021	1153	93.65

TABLE III

Liquid Propyl Alcohol and Water

Temperature 26°.00C

No.	Volume % of water in total of mixture	Density (in gms./cc.)	Velocity (metre per sec.)	Adiabatic compressibility $\times 10^{-6}$
1	50	.9241	1459	50.86
2	60	.9417	1502	47.11
3	70	9588	1552	43.28
4	80	.9749	1592	40.46
5	90	.9855	1558	41.82
6	100	.9968	1500	44 59

atom, that this second electron begins to move in phase with the first, and as result attraction ensues.

The specific formulae for this mutual interaction energy, giving its numerical value, have been calculated for a very small number of only simple atoms or molecules, notably helium. The formula in its simplified and approximate form is

$$E = -\frac{3}{4} \cdot \frac{\alpha^2 V}{R^6}$$

where E is interaction energy,
α is polarisability,
R is distance between two interacting molecules,
V is excitation potential and may be taken as the ionisation potential.

For two different molecules

$$E = -\frac{3}{4} \cdot \frac{\alpha_1 \alpha_2 V}{R^6}.$$

Induction forces:—If one molecule is unsymmetrically charged, *i.e.*, is a permanent dipole, then the field produced by it on another molecule or part of it so deforms its electronic configuration that it becomes an 'induced' dipole of magnitude $M = -\alpha F$ where F is the field of the inducing molecule and α (a constant) is the polarisability of the induced molecule. The approximate formula for interaction is

$$E = -\frac{2\alpha\mu^2}{R^6}$$

where μ is permanent dipole moment of the molecules.

If the two molecules are dissimilar of moments μ_1 and μ_2 and polarisabilities α_1 and α_2 then

$$E = -\frac{1}{R^6}[\alpha_1\mu_2^2 + \alpha_2\mu_1^2].$$

Orientation or Keesom forces:—Two molecules having permanent dipoles are so orientated under their mutual action that their potential energy becomes negative, *i.e.*, they tend to attract each other. The formula for the potential energy is

$$E = -\frac{2}{3}\frac{\mu^2}{R^6} \cdot \frac{1}{RT} \text{ for } kT >> \frac{\mu^2}{R^3}$$

and

$$E = -\frac{2\mu^2}{R^3} \text{ for } \frac{\mu^2}{R^3} >> kT$$

where K is Boltzmann's constant and T absolute temperature. For unlike molecules of moments μ_1 and μ_2 the corresponding formulae become

$$E = -\frac{2}{3}\cdot\frac{\mu^2\mu_2^2}{R^6}\cdot\frac{1}{kT} \text{ and } E = -\frac{2\mu_1\mu_2}{R^3}.$$

Now it is clear from the above formulae that all the type of forces are extremely short-range ones. In liquids, therefore, where the distance among the atoms of different molecules are comparable to the length of dipoles, it is misleading to think of Keesom forces in terms of the total dipole moment of a molecule or molecules. It is imperative to consider the individual dipoles of a molecule, their moments and their positions with respect to the whole molecule. For example in *p*-dichlorobenzene, the net dipole moment is zero but actually there are two strong dipoles $c-d$ which will play an important part in intermolecular forces.

Again, ethers, esters, nitrobenzene are all polar having quite large moments but still have not much Keesom energy due to the dipoles being effectively screened. In alcohols the O—H dipole has a dipole moment of 1 >D (much less than of nitrobenzene 4 D) and is on the surface of the molecule. Due to these reasons alcohols have large Keesom or orientation energy and in fact their pronounced association is due to the great activity of their dipoles.

In water, the dipole energy contributes nearly the whole of energy due to the special structure of its molecule. The molecule has two dipoles, open on both the sides for strong intermolecular action.

Cohesive energy and compressibility.—It can be seen from simple considerations that cohesive energy and compressibility are inversely related.

The kinetic energy of molecules due to temperature tend to make the molecules fly apart, while the cohesive energy tend to knit them as close as possible.

(*Note.*—We will neglect the repulsive energy which has also been recognised, due to it being an extremely short-range one, *i.e.*, falling off with about 11th or 12th power of the distance.)

The molecules will come in a dynamic equilibrium position where the potential energy is minimum. The greater the cohesive energy the nearer the molecules will be in their equilibrium position. Since the cohesive energy falls off inversely as the distance, in fact with inverse sixth power of the distance, the nearer the molecules in equilibrium the more rapid will the energy change on either side of this position. This indicates that the higher the cohesive energy the more difficult it will be to move a molecule from its equilibrium position and accordingly the compressibility will be low. To put it in other words, the higher the cohesive energy, the higher the internal pressure, and from this view point the compressibility naturally becomes small.

In fact, Bridgman [6] has actually found that liquids of high cohesive energy, *e.g.*, for glycols, and glycerols (due to their independent OH dipoles) the compressibility is extremely small.

COMPRESSIBILITY AND NATURE OF MIXTURES

If the two unlike molecules are otherwise similar in shape and structure, the compressibility change with change in the composition is expected to fall along the graph for the ideal law for mixtures, *i.e.*, all the points on the graph representing the compressibilities of the different compositions of a mixture will lie on the straight line joining the two points corresponding to the compressibilities of the two pure liquids.

The departure from the ideal case can occur in the following cases:

(1) The molecules have very different shapes, so that the forces between them cannot be taken as the average or geometrical mean of the forces between like molecules.

(2) The two unlike molecules break up the associations that were present in the pure liquid, or form associations of their own.

(3) The two liquids have different magnitudes of contributions to the different kinds of energies making up the total cohesive energy, *e.g.*, in a mixture of polar and non-polar liquid.

In the present state of knowledge of molecular forces which is very approximate, it is not possible to treat our problems quantitatively except in a few special cases, *e.g.*, the case of alcohols and water in this paper.

MIXTURE OF ALCOHOLS AND WATER

As has already been mentioned, both alcohol and water molecules have O—H dipoles and their positions with respect to the shape of the molecules is such that their field is very great for intermolecular action. Due to their active dipoles, the two liquids in their pure forms are highly associated. It is more so in water than in alcohol due evidently to there being no chain as in the latter. The existence of association has been directly shown by infra-red absorption spectra,[7,8,9,10] by dielectric polarisation measurements[11] and by X-ray measurements.[12]

Now any associated group will have its component molecules so orientated relatively, that their net dipole moment for outside field is very small, tending to zero. The associated group will be well knit up in itself, difficult to break up, and there will not be much interaction energy among the different associated groups. In sound wave propagation it is the associated groups as a whole that move to and fro, and so the compressibility measured in our case is that related to cohesive forces among the associated groups as a whole and also among those molecules which are free. If the associated groups are broken up by some means, the individual dipoles will be free creating a strong intermolecular field and low compressibility.

Now as water and an alcohol are mixed, the associations in both the liquids are broken up and there prevails random distribution. The evidence for this has been deduced from the following cases:

(1) The partial vapour pressures of the components of water-alcohol mixtures were determined by Martin and Brown.[13] Raolt's Law for ideal mixtures (*i.e.*, where there is random motion and distribution of the molecules) was found to hold for nearly the whole range of concentrations, the divergence being in very dilute aqueous solutions. At this extreme end, water was supposed to have the sub-crystalline structure, but otherwise there was evidence of complete random distribution.

(2) *Dielectric polarisation.*—Wyman [14] investigated the dielectric polarisation of ethyl alcohol-water mixture and found that the additivity rule held throughout all ranges of concentration. Now this can be so if the constituent dipoles contribute to the total polarisation, independently of the presence of other dipoles. Hence in these mixtures there is completely random distribution of molecules.

(3) *Spectroscopic evidence.*—It has been established that in associated polar liquids like water depolymerisation is produced by heating the liquid. On depolymerisation the infra-red or Raman frequencies of the O-H bands are shifted to a higher value. For water-alcohol mixtures the evidence is meagre. However, Bars and Cranen[15] have shown in rather a rough way that the water band is shifted to a higher frequency on mixing it with alcohol. They took two percentages 50% and 25% of alcohol by volume in water and found that the shift is maximum for 25% mixture. The exact interpretation of this result may not be forthcoming yet but it shows in a qualitative way that depolymerisation is produced.

(4) Butler, Thomson and Maclennan[16] measured the partial vapour pressures of aqueous solutions of homologous aliphatic alcohols and attempted to account for the main features of the behaviour in terms of the cohesive energy between the molecules. Langmuir, by using his postulate of "principle of independent surface action,"[17] has shown how the intermolecular energy in a liquid can be obtained by summing the interfacial energies of the various surfaces of contact of the molecules.

On the assumption that the molecules are distributed entirely at random, he obtained for a binary solution of two substances A and B an equation for activities:

$$\log f_A = \frac{\beta^2 S_A \phi}{kT} \quad \text{and} \quad \log f_B = \frac{\alpha^2 S_B \phi}{kT}$$

where S_A and S_B are the surface areas of molecules A and B respectively, α and β their surface fractions in the solution, f_A, f_B their activities, and ϕ the "mixture energy." By the mixture energy ϕ is meant the work done to bring a molecule A from its pure liquid into the pure liquid of B, or to bring the molecule B from its pure liquid state into the pure liquid of A.

The above equation accounted for not only the main difference between one alcohol and another, but also for the variation of the activity coefficients over the greater part of the range of concentrations. The divergence from the equation

which occur in very dilute aqueous solutions may be due to the failure of the assumption of an entirely random distribution and orientation of molecules in these solutions. Hence we can consider that in a mixture of alcohols (particularly lower alcohols) and water, the molecules are all randomly distributed, that is, there is no grouping in any of the constituents.

Now Butler[18] in connection with a paper on entropies and heats of hydration of alcohols has obtained the energy of binding of a water molecule to another water molecule as also to OH or CH_2 groups, etc. of an alcohol molecule. As this energy relationship is required in later work, this is given here in some detail. Starting from Langmuir's[17] principle of independent surface action in solutions and Bernal and Fowler's[19] thesis of pseudo-tetrahedral structure of water molecules, he considers that when a solute molecule has to be introduced in water, a cavity has to be made large enough to hold the water molecule and then the solute molecule can be introduced in that cavity. Considering only the forces between adjacent molecules the energy ϕ required for introduction may be put as

$$\phi = \frac{n}{2}\gamma_{W-W} - \Sigma a\,\gamma_{A-W}$$

where γ_{W-W} is the energy required to separate a single pair of water molecules and n is the total number of water molecules thus separated, γ_{A-W} is the energy of interaction of the group A in the solute molecule with an adjacent water molecule and 'a' is the number of water molecules adjacent to the group.

Thus one can write

(1) $$\phi_{CH_4} = 2\gamma_{W-W} - 4\gamma_{CH-W}$$

(2) $$\phi_{C_2H_6} = 3\gamma_{W-W} - 6\gamma_{CH-W}.$$

From these one obtains

(3) $$\phi_{CH_2} = \phi_{C_2H_6} - \phi_{CH_4} = \gamma_{W-W} = 2\gamma_{CH-W}$$

where ϕ_{CH_2} represents the energy of solution for the CH_2 group only. Knowing the experimental value for the heat of hydration of methane and ethane this was obtained by Butler as $\phi_{CH_2} = -1.58$ k.cal. The value of γ_{W-W} can be easily obtained from the heat of vaporisation of water. This is 10.5 k.cal. at 25°C. Since the removal of a water molecule from its surroundings means the breaking up of 4W—W bonds (water having a tetrahedral structure), and since these four broken water linkages will reunite in 2W—W bonds again, the heat of vaporisation being the difference of energy in the two cases is equal to $2\gamma_{W-W}$. Thus the value of γ_{W-W} is obtained as 5.25 k.cal. Putting this value of γ_{W-W} in equation (2) or (3) and considering the experimental values of $\phi_{C_2H_6}$ and ϕ_{CH_2} one obtains the

value of $\gamma_{CH-W}=3.36$ or 3.42 which agree fairly well. The agreement shows that this method of calculation of the bond energy is tenable.

Butler then obtained the energy values of γ_{OH-W} by considering the case of ethyl alcohol. One can consider

$$\phi_{C_2H_5OH}=4\gamma_{W-W}-5\gamma_{CH-W}-3\gamma_{OH-W}.$$

Putting the values of γ_{W-W} and γ_{CH-W} obtained before and the experimental value of $\phi_{C_2H_5OH}=12.88$ k.cal., one finds $\gamma_{OH-W}=5.6$ k.cal.

Thus the value of γ_{OH-W} is greater than that of γ_{W-W}.

This leads to the conclusion that the OH group of alcohols have got greater attraction for water molecule than the mutual attraction between two water molecules themselves. The alcohol molecules can therefore break up the water associations. Consequently the cohesive energy increases by the addition of water to alcohol. Hence the compressibility curve should always lie below the straight line corresponding to the linear law.

Considering the equation

$$\phi_{CH_3OH}=3\gamma_{W-W}-3\gamma_{CH-W}-3\gamma_{OH-W}$$

we find

$$3\gamma_{W-W}=5.25\times 3=15.75 \text{ k.cal.}$$

$$3\gamma_{CH-W}+3\gamma_{OH-W}=3(3.36)+3(5.6)=26.88 \text{ k.cal.}$$

This shows that cohesive energy is increased when a molecule of methyl alcohol is introduced in water and gets surrounded by 6 molecules of the latter. From the molecular weights of CH_3OH and H_2O and their densities at the required temperature, the volume percentage of methyl alcohol required for the least compressibility of water-alcohol mixture can be calculated. In this case we require six molecules of water for each molecule of $CH_3.OH$.

Similar calculations can be made for ethyl and propyl alcohols. A comparison of the calculated and experimental values is shown in the next table.

Alcohol	Ratio of molecules of alcohol to those of H_2O	Weight percentage of alcohol	Volume percentage of alcohol calculated	Volume of alcohol observed
Methyl	1 : 6	22·9	27·3	26-27
Ethyl	1 : 8	24·2	29·3	28-29
Propyl	1 : 10	25	28·8	19

The results show that for methyl and ethyl alcohols, there is close agreement between the calculated and the observed values, while for propyl alcohol there is an appreciable departure to the extent of about 10%.

The agreement in the case of the first two alcohols shows that the basic postulates (*viz.*, Langmuir's principle of independent surface action and Bernal and Fowler's thesis about structure of water) for the energy equation are sound and that the reason for the departure in propyl alcohol-water solution must be looked for in some other direction.

Now the volume computation from the energy equation

$$\phi_{C_3H_7OH} = 5\gamma_{W-W} - 7\gamma_{CH-W} - 3\gamma_{OH-W}$$

is based upon the obvious assumption that each molecule of the alcohol is surrounded by ten molecules of water, that there are no other molecules of water which do not surround any of the alcohol molecules, and that the alcohol molecules do not aggregate.

If there is some sort of aggregation of alcohol molecules the volume computation must fail. The following is meant to show how far we can depend upon the assumption of non-aggregation of alcohol molecules. Considering pure alcohols we find that as the chain length increases, their viscosities increase and solubilities in water decrease. This has been recognised as due to increasing chain to chain aggregation of alcohol molecules with increasing chain length for it leads to lowering of potential energy. When these alcohols are added to water, the tendency of chain to chain contact will detract from the degree of solubility. Also as has been seen $\gamma_{CH\text{-}W} = 3.25$, $\gamma_{W\text{-}W} = 5.2$ k.cals., showing that CH groups tend to remain away from water, *i.e.*, are hydrophobic. This property of CH groups is well known in the investigation of behaviour of layers on water of insoluble alcohols. In the smaller chain alcohols the hydrophilic power (water-attracting powers) of OH groups predominates and they are therefore highly soluble and in the higher chain alcohols, the hydrophobic powers of the CH groups predominates, leading to aggregation of the alcohols in water, with consequential decrease of solubility. We can expect on these grounds that as the chain length increases, the departure in our calculations and in others (*e.g.*, on solubility) will be comparatively sudden, for by the addition of a single CH_2 group the alcohol as a whole may be changed from hydrophilic to hydrophobic, the non-aggregation giving place to aggregation. Bury and Hartley [20] have investigated the phenomena of micellar aggregates in aqueous solutions. Their results indicate that clustering of fatty acids and alcohols seems to begin at butyric acid and alcohol. In our case it seems to begin even at propyl alcohol.

Again the halogen alkyl amines $Cl\cdot CH_2\text{-}(CH_2)_{n-2} - CH_2 - NH_2$ are liquids miscible with water. The lower members of this series are completely miscible. Solomon [21] has found that whereas for $n=5$ the solubility certainly exceeds 1 mol/litre, it drops by more than two hundredfold (solubility .005 mol/lit.), when $n=6$. The author tries to interpret this observation by the aid of Langmuir's principle. For $n=5$, the hydrophilic power of the amino group

preponderates as opposed to the hydrophobic power of the alkyl residue but when $n=6$, this is no longer the case.

Hence it is not surprising (on the other hand expected) that we have a parallel sort of date in compressibilities. Up to ethyl alcohol the energy equation used gives accurate results, but in the next higher (*i.e.*, propyl) alcohol, the calculated percentage of alcohol for minimum compressibility is too high.

We can reason out the difference in behaviour of methyl and ethyl alcohols from the propyl, by also considering their molecular structures.

Methyl alcohol (CH_3OH) cannot be taken as a chain compound at all. It may be thought of as derived from methane CH_4 by the substitution of one H by OH. Now CH_4 is tetrahedral in shape due to the tetrahedral character of the carbon valencies and CH_3OH may be taken on the whole to be of the same structure. Due to the tetrahedral sort of structure of water, any foreign molecule or ion tetrahedral in shape will fit in better in the structure of water than that of any other shape. Frank [22] has shown from entropy considerations that ions NH_4^+, SO_4^- fit in the structure of water while NO_3^-, Cl^-, Br^-, etc., do not.

So, although the CH groups are hydrophobic, but due to the tetrahedral shape of the molecules, they will nevertheless interact with water efficiently and due to this and the fact that the hydrophilic power of OH group is comparatively strong, and that there is little or no chain character, there will be no tendency for chain-to-chain aggregation. In this case energy equation will yield the correct percentage of alcohol.

In ethyl alcohol $CH_3.CH_2.OH$, a chain has been formed but the CH_3 group as a whole may be taken tetrahedral in character and so able to interact with water. The two CH's of CH_2OH will interact with water due to the following reason :—

The group CH_2OH as a whole may be taken as conforming to the tetrahedral sort of shape, being derived from CH_3.

Due to the above and also because the chain length is not big after all, there will be no tendency for aggregation and the energy equation will give the right percentage.

With propyl alcohol the picture is different. In $CH_3.CH_2.CH_2OH$, the CH_3 and CH_2OH will behave as before but the middle group CH_2 isolated as it is from the influence of OH and not tetrahedral in shape, will show little tendency to react with water due to its inherent hydrophilic nature. Due to this significant reason, and that the chain length has increased, there will be a suddenly increased tendency to self-aggregation.

This sudden difference of behaviour of propyl alcohol from that of lower alcohols has been reflected in our compressibility data by the abrupt deviation between the ideal calculation and observation.

The energy equation shows, as has been said somewhere before, that the cohesive energy increases as a molecule of alcohol is introduced and gets

surrounded by water molecules. So, we have the conclusion that the cohesive energy will be the greatest, when there are the greatest number of alcohol molecules such that each molecule of alcohol is completely surrounded by 10 water molecules, at the same time the distance between the alcohol molecules being sufficient so that they may not be expected to stick together in aggregation. The ideal computation, *i.e.*, 30% of alcohol, corresponds to the case when the alcohol molecules, are just separated from each other by these surrounding water molecules, and that there are no excess molecules of water not occupied in surrounding alcohol molecules. Since this behaviour (*i.e.*, non-aggregation) is not expected to hold for this high percentage, on the grounds presented above, the percentage volume of alcohol must be reduced till it is just sufficient to keep the molecules of the alcohol in non-aggregation. At this lower percentage then (*i.e.*, 19% in the actual case) one will have the minimum compressibility.

After the results had been obtained, the author came across two papers, [23,24] where velocities in ethyl alcohol water mixtures are measured. The results, however, were given without any attempt at theoretical treatment.

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Bose Research Institute,
Calcutta

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